An LED Approach for Measuring the Photocatalytic Breakdown of Dye on Titanium Dioxide Coated Surfaces

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ABSTRACT

A simple method to estimate the photocatalytic reactivity performance of spray-on titanium dioxide (TiO_2) coatings for transmissive glass surfaces was developed. This novel technique provides a standardized method to evaluate the efficiency of photocatalytic material systems under a variety of illumination levels. To date, photocatalysis assessments have generally been conducted using mercury black light lamps. Illumination levels for these types of lamps are difficult to vary, consequently limiting their use for assessing material performance under a diverse range of simulated environmental conditions. This new technique uses a stable ultraviolet (UV) gallium nitride (GaN) light emitting diode (LED) array instead of a traditional black light lamp to initiate and sustain photocatalytic breakdown. This method was tested with a UV-resistant dye (Crystal Violet) applied to a TiO_2 coated glass slide. Experimental control is accomplished by applying Crystal Violet to both TiO_2 coated slides and uncoated control slides. A slide is illuminated from the dye side by the UV LED array at various light levels representative of outdoor and indoor conditions. To monitor degradation of the dye over time, a temperature-stabilized white light LED, whose emission spectrum overlaps with the dye absorption spectrum, is used to illuminate the opposite side of the slide. Using a spectrometer, the amount of light from the white light LED transmitted through the slide as the dye degrades is monitored as a function of wavelength and time. In this way, the rate of dye degradation for photocatalytically coated versus uncoated slide surfaces can be compared. Results demonstrate that the dye transmission increased much more rapidly on the photocatalytically coated slides than on the control uncoated slides, and that dye degradation is dependent on illumination level. For photocatalytic activity assessment purposes, this experimental configuration and methodology minimizes many external variable effects and enables small changes in absorption to be measured. This research demonstrates the use of this alternative, innovative LED light source design over traditional mercury black light lamp systems and non-LED lamp approaches. This novel technology begins to address the growing need for a standard method that can assess the performance of photocatalytic materials before deployment for large-scale, real world use.

INTRODUCTION TO PHOTOCATALYSIS

In the presence of UV light (320–400 nm) and water, the photocatalyst TiO_2 has two unique qualities:

1. **Breakdown Properties**–accelerated decomposition of compounds:
   - Organic and inorganic compounds (i.e., Volatile Organic Compounds-VOCs, Polychlorinated Biphenyls-PCBs, pesticides, Nitrogen Oxides-NO_x)
   - Antimicrobial/antibactericidal (i.e., bacterium, fungi, viruses)
2. **Self-Cleaning Properties**–creates highly washable surface state:
   - Contact angle between the photocatalyst surface and water is reduced
   - Induces superhydrophilicity

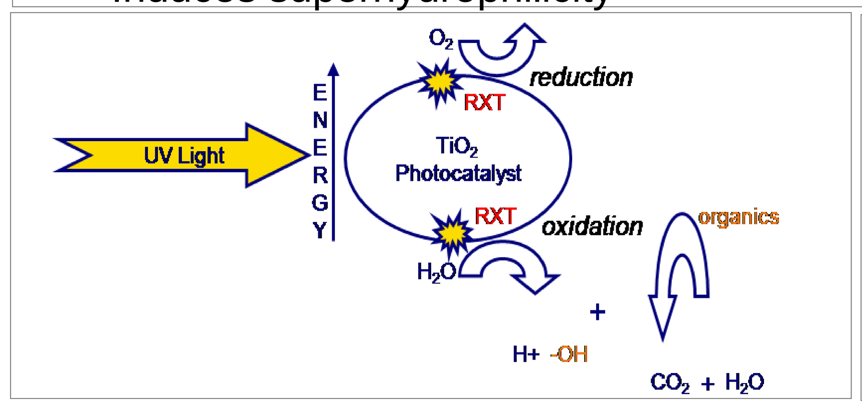


Figure 1. Photocatalysis

Reduction-oxidation reaction occurs at the surface of the catalyst and generates:

- -OH, hydroxyl radicals and
- O^-_2, superoxide ions

These molecules break down the structure of the microorganisms and of inorganic and organic (VOCs) compounds and convert them into CO_2 and H_2O.

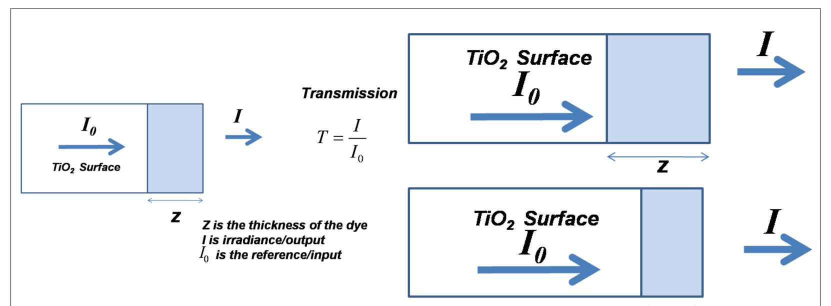
PROBLEM AND PROPOSED SOLUTION

Problem: Limited data available on performance of commercially available photocatalytic materials under a variety of environmental conditions.

Solution:

- Time series transmission spectra of dye breakdown are taken to determine photocatalytic reactivity.
- Crystal Violet dye used to assess degradation capability (use of other dyes may also be possible).
- Traditional UV simulator black light lamp replaced with a GaN UV LED array to allow for variation in light level.

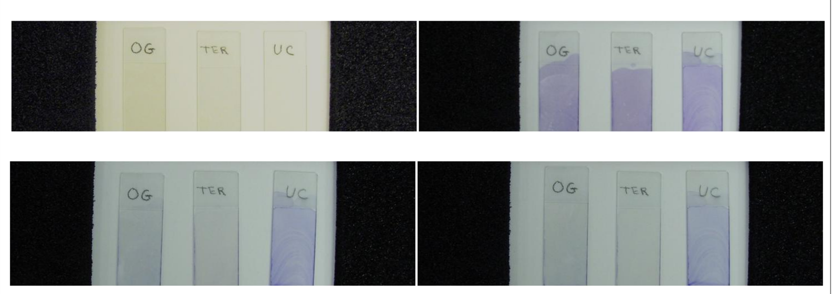
Figure 2. Transmission Through Dye



Transmission will increase as the dye breaks down

***Note the reduction in Z is only part of the story; absorption can be reduced due to several processes (i.e., chemistry).**

Figure 3. Dye Degradation



Top left: slides pre-dye application.
Top right: slides post-dye application.
Bottom left: slides 1 hour post UV exposure.
Bottom right: slides 1.5 hours post UV exposure.

EXPERIMENTAL METHOD

This study examined the photocatalytic breakdown of Crystal Violet, a strongly absorbing dye that is relatively insensitive to direct UV photodecomposition. After the application of the dye, the slide was exposed to UV radiation and illuminated from below with a temperature-stabilized white light Cree, Inc., LED. The white light LED produces light from approximately 420–800 nm, which overlaps well with the Crystal Violet absorption spectrum. The LED was powered by a constant current source and temperature stabilized to 20 ºC with a thermoelectric cooler system, producing a light source that was stable to better than 0.1% over several hours. A calibrated Analytical Spectral Devices, Inc., Full Range (350–2500 nm) spectroradiometer was used to measure the transmission of white light through the slide over time. See schematic design in Figure 4.

Figure 4. Transmission Experiment Schematic

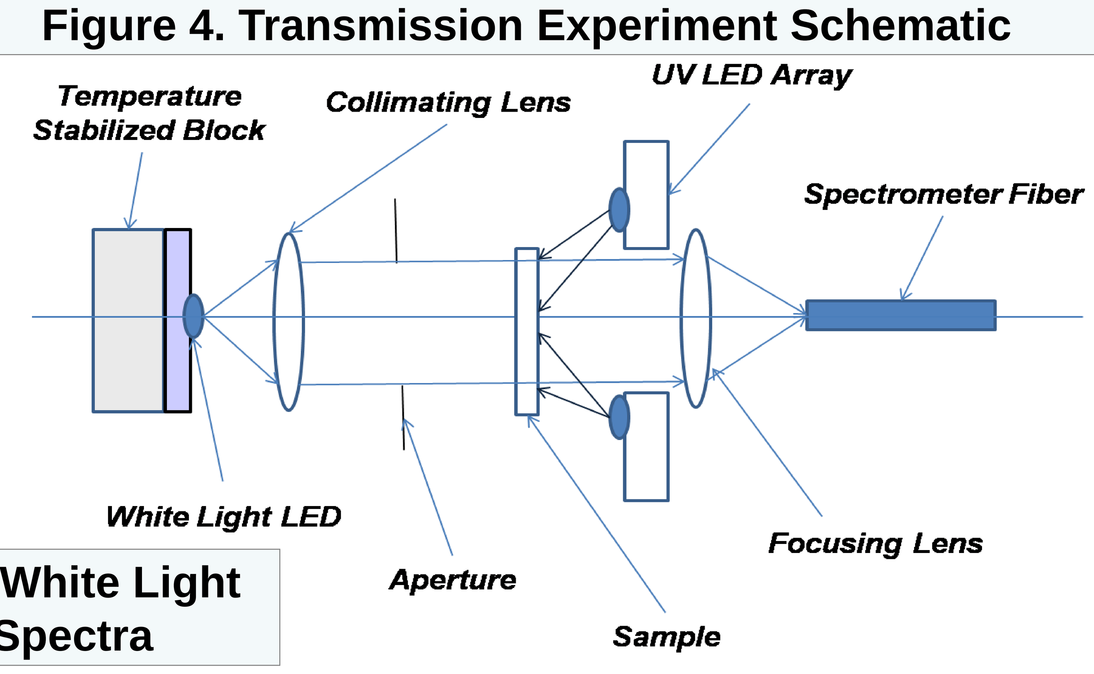
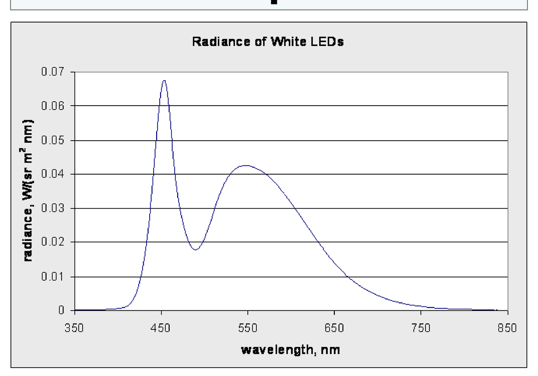


Figure 5. White Light LED Spectra



White Reference LED: Temperature-stabilized white light LED produces a light source that is stable <0.2% over days and allows for one reference measurement to be made. Spectra emission does not produce UV light and overlaps well with Crystal Violet absorption.

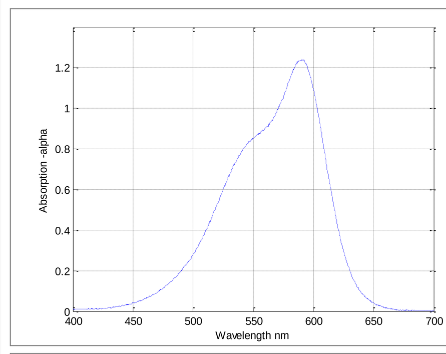
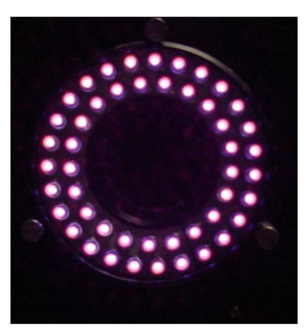
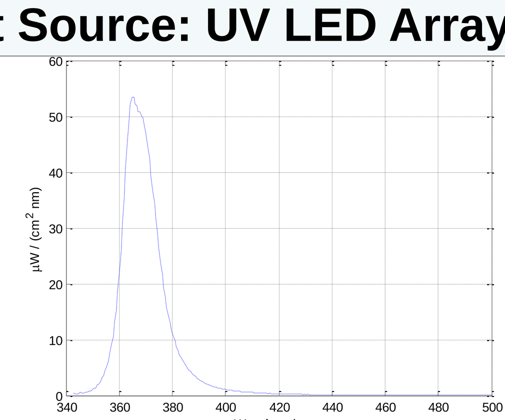


Figure 6. Crystal Violet Dye Absorption Spectra

Crystal Violet Dye: absorption is in the visible wavelengths; relatively insensitive to UV photodissociation

Figure 7. Light Source: UV LED Array

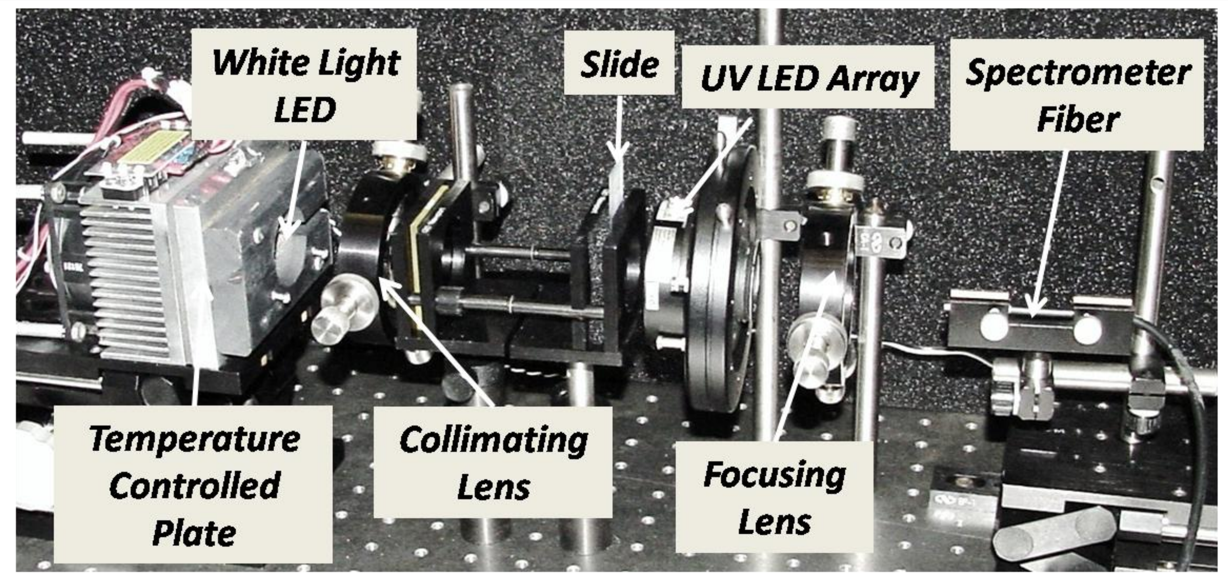




- DC-powered continuous light source
- Intensity can be easily adjusted

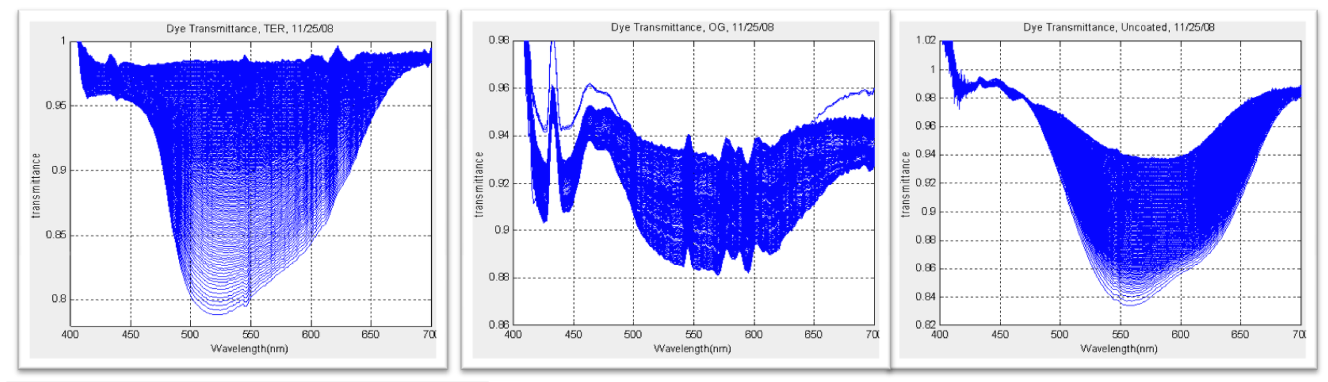
EXPERIMENTAL SET-UP

Figure 8. Illumination Approach with UV LED Array



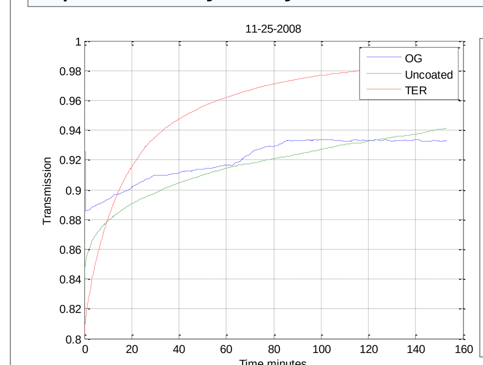
RESULTS

Figure 9. Transmission Spectra Time Series



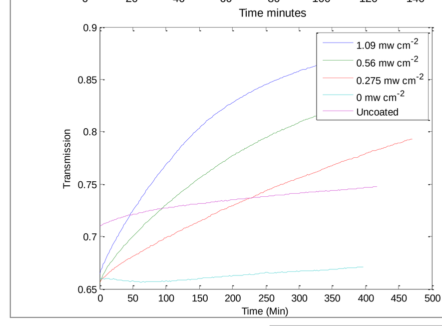
Nanocepts, Inc. photocatalytically coated slide | Uncoated slide | PURETi photocatalytically coated slide

Measurements taken with standard UV lamp (not an LED array) transmission increasing with increased time.



Peak Absorption Transmission Time Series:

- Irradiance 59 Watts/m^2
  Similar to noon-time on a summer day
- Transmission at 550 nm plotted
- Three different slides: Nanocepts TER-10 photocatalytic coating (red); PURETi OG photocatalytic coating (blue); uncoated (green).



Vary Light Level Example:
Transmission at 550 nm shows increasing dye breakdown with increasing UV irradiance using the TER-10 coated slides.

SUMMARY

1. **A simple method for evaluating photocatalytic titanium dioxide reactivity under different lighting conditions is under development.**
2. **UV LED sources allow for simple control of light level.**
3. **White light LEDS have spectra that overlap the Crystal Violet absorption spectrum and many other dyes.**
4. **Initial studies have demonstrated stability and repeatability of experimental set-up and design.**

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